AN ANALYSIS OF MERCURY (HG) LEVELS IN RIVER WATER AROUND THE GOLD MINING AREA IN BANYUWANGI REGENCY

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Abstract.

Mercury (Hg) is a metal that is commonly found in water and has toxic properties, so it is very dangerous for human health and the environment. Mercury in the environment can come from gold mining activities such as in Pesanggaran Village, Banyuwangi. Based on information from the surrounding community, the waste disposal flowed into the river and it was feared to affect the quality of river water in this area. This study aimed to analyze the mercury level in the river water using the UV-Visible Spectrophotometer method, where river water samples were taken from the upstream, middle, and downstream parts. Determination of mercury levels was carried out at the STIKES Banyuwangi Laboratory. The results showed that the Hg content in the river water around the gold mining area of Pesanggaran Village, Banyuwangi ranged from 0.031 to 0.033 mg/L. The Hg level of river water in this area was above the threshold and it was not recommended to use as drinking, bathing, cooking or washing. However, it is necessary to analyze Hg levels using other methods, such as the AAS (Atomic Absorption Spectroscopy) method which is more expensive but more accurate results will be obtained.

Keywords: Mercury, UV-Visible Spectrophotometer, River Water, Gold Mining

1. INTRODUCTION

Water is a natural resource needed in life to meet daily needs (Auliyah et al., 2019). One source of water that is often used by the community in various activities is river water (Ayuningtyas and Yunita, 2014). There are various kinds of substances in river water, one of which is in the form of heavy metals (Rai, 2019). Heavy metals are toxic to living things, even though they are actually toxic or non-toxic depending on the levels of these substances. If there are toxic substances in dissolved water or other substances that interfere with the designation of water, then the water is said to be polluted (Febrianti et al., 2018).

Heavy metals can be chromium (Cr), lead (Pb), mercury (Hg), zinc (Zn), copper (Cu), and so on (Qomariyah, 2014). The sources of heavy metals found in water come from nature (volcanic dust, rock erosion, etc.) and human activities (domestic and industrial waste, etc.) (Maddusa et al., 2017). One of the toxic heavy metals is mercury (Hg) (Mahmud et al., 2020.). Mercury is a metal that is usually used in gold mining to separate gold ore from rocks till the refining process (Qomariyah et al., 2021).

In Pesanggaran Village, Banyuwangi there is a river that is often used by local residents for activities ranging from bathing, washing, toileting, washing clothes, washing household furniture to irrigating fields. The river located is close to gold mining location which utilizes the heavy metal mercury (Hg), so it has the potential to produce waste. Based on information from the surrounding community, the waste disposal flows into the river and it is feared to affect the quality of river water in this area.

The Methods for determining mercury levels in water samples have been developed (Pratiwi and Aida, 2018; Suteja et al., 2018). The AAS (Atomic Absorption Spectroscopy) is a metal analysis method that has been widely used because it produces accurate results compared to other methods (Nuryono et al., 2019; Qomariyah and Hidayah, 2021). However, there are not many AAS tools in Indonesia, so they are quite expensive (Ohi et al., 2020; Trisna, 2018). Therefore, we used the UV-Visible Spectrophotometry method which is cheaper and is expected to obtain accurate results (Kustiningsih et al., 2017; Susanti et al., 2014). However, in the analysis using this method, a complexing solution is needed so that the sample can form complexes and produce colors as a condition for being read by UV-Visible Spectrophotometer (Subhi and Sumijanti, 2021). Several kinds of complexing compounds have been widely used in previous studies, such as ditizone (Huljani and Rahma, 2019) and ARS-12 (Nasir, 2018). There were still few studies using Ethylene Diamine Tetraacetic Acid (EDTA) as a complexing agent. Thus, in this study EDTA was used as a complexing compound. In addition to see the performance of EDTA, the price is relatively cheap.

Based on the problem above, a study was conducted to determine the mercury level (Hg) found in river around the gold mining industrial area of Pesanggaran Village, Banyuwangi using UV-Visible spectrophotometer method. With the hope, the mercury levels of river water can be known so that the quality of the river water can be known.

2. RESEARCH METHOD

2.1. Tools and Materials

The tools used in this study were a UV-Visible Spectrophotometer (Genesys 10S UV-VIS), analytical balance (Mettler Toledo), 5 mL measuring cup (Pyrex), watch glass, stir bar, sample bottle, funnel, measuring flask. 100mL (Iwaki), and a 100mL beaker (Pyrex). The materials used were aquades, 0.1 M sodium hydroxide (NaOH), 37% hydrochloric acid (HCl), mercury (II) sulfate (HgSO4), EDTA-4Na (Ethylene Diamine Tetra-acetic Acid) 0.05 M and 0.1 M, and river water samples.

2.2. River Water Sampling

Samples were from river water around the gold mining industry area in Pesanggaran Village, Banyuwangi Regency which was taken from several points of liquid sampling technique. Sampling points in water bodies must be representative (upstream, middle, and downstream) with a depth of 1 meter. The method was carried out by pulling it with a sample bottle at a depth of 1 meter. Sampling was carried out repeatedly, in which the first collection was used to clean the sampling bottle and then discarded. The second collection was the water sample to be examined, filled into the sample bottle and then closed with the sample bottle cap. Samples were taken in the morning at 08.00 WIB on June 2, 2022. The samples were put in sample bottles, labeled, stored in boxes and analyzed at the Chemistry Laboratory of STIKes Banyuwangi

2.3. Optimum pH Determination

The standard Hg solution with a concentration of 2 ppm was varied at pH = 4 to pH = 11 using 0.1 M NaOH solution, or concentrated HCl was added to obtain the appropriate pH. Next, 1 mL of 0.1 M EDTA and 1 mL of each were added to these solutions. The standard solution that had been added with EDTA was left for ± 30 minutes, then

measurements were made using a UV-Visible spectrophotometer at a wavelength of 404 nm.

2.4. Determination of Hg and EDTA Levels Using UV-Visible Spectrophotometry

A certain volume of 100 ppm Hg standard solution was put into a 50 mL volumetric flask to obtain concentration variations of 1, 2, 3, 4 and 5 ppm. Take 10 mL of each solution with this concentration and add 1 mL of EDTA and 15 drops of 0.1 M NaOH. Then, HCl was added according to the optimum pH obtained. Furthermore, the absorbance determination of the standard solution using the maximum wavelength was carried out. The measurements obtained from the standard solution were then made a calibration curve.

2.5. Linearity Test

The preparation of calibration series was made using a blank matrix in which standard analytic of known concentration was added quantitatively. The concentrations made include five concentrations, namely 1, 2, 3, 4 and 5 ppm. Then the linear regression equation was determined so that the R2 value was close to 1. The standard Hg solution with a concentration of 2 ppm was varied with pH = 4-12 using 0.1 M NaOH and 1 mL of 0.01 M EDTA was added.

2.6. Measurement of Hg Levels in River Water Samples by UV-Visible Spectrophotometer

Analysis of river water samples using a UV-Visible spectrophotometer was carried out by taking 10 mL of each sample obtained from the upstream, Middle, and downstream of River. Each sample was added 1 mL of 0.01 M EDTA solution and 15 drops of 0.1 M NaOH solution. The solution was allowed to stand for 30 minutes and then its absorbance was measured at a wavelength of 404 nm.

3. RESULTS AND DISCUSSION

3.1. Optimum pH Determination

Optimum pH determination was carried out with the aim of obtaining a stable pH for the formation of Hg and EDTA complexes. EDTA was used as a reagent for the determination of metals number. EDTA was used to bind metal ions under the right conditions. The reaction for formation of the Hg-EDTA complex was shown in Figure 1.



Figure 1. The reaction of EDTA with Hg

This Hg-EDTA complex compound was prepared by reacting a solution of Hg2+ with EDTA at pH = 4-11. The maximum absorption value depended on the pH used. Each solution with a different pH was measured at a wavelength of 404 nm. At each pH, a different maximum wavelength was obtained. The optimum pH value and maximum wavelength obtained were presented in Figure 2.



Figure 2. Optimum pH chart

In Figure 2 above, it was known that the optimum pH obtained was pH = 5 with an absorbance of 0.69 and the maximum wavelength obtained was 404 nm. At pH = 5, a stable complex was formed between Hg and EDTA. The maximum wavelength obtained at this pH was used to obtain sensitive and accurate analytical results.

3.2. Making a Calibration Curve Using UV-Visible Spectrophotometer

Making a calibration curve was done by using concentration variation of standard Hg solution. The concentrations used were 1, 2, 3, 4, and 5 ppm, where 1 mL of EDTA reagent was added to each standard solution. In the formation of complex with EDTA, a purplish complex solution was formed due to EDTA changes colour depending on the solution pH.

In our research, the optimum pH was at pH = 5, in which after measuring the pH, we obtained a solution that corresponded to pH = 5, so no acid (NaOH) or base (HCl) was added.

After the solution was mixed with the reactants, the complex could be seen immediately and the colour intensity would increase up to 30 minutes and would be constant for up to 90 minutes. Therefore, 30 minutes was the optimum time for a stable complex to form. The calibration curve for the Hg standard solution obtained was presented in Figure 3 below.



Figure 3. Hg Standard Calibration Curve

3.3. Validation of Hg Determination Method with UV-Visible Spectrophotometer

The linearity of an analytical method was obtained by making four different concentrations of standard mercury so that it can describe the correlation between the concentration and absorbance. Increasing the concentration of the standard solution will result in a large absorbance as well.

The concentration variations used were 1, 2, 3, 4 and 5 ppm. The measurements were taken to obtain a linear regression curve, namely y = -0.0404x + 0.1374 with an R2 value of 0.9958. The analytical method met the accepted linearity requirements because it was greater than 0.9950. This showed that the method produces good linearity.

3.4. Determination of Hg Levels in River Water Using a UV-Visible Spectrophotometer

Measurement of Hg concentration in Pesanggaran River water was carried out by UV-Visible Spectrophotometer to produce concentration values presented in Table 1 below.

Sample	Hg level	Normal Value according to the Indonesian Ministry of Health
1	0,031 mg/L	0,005 mg/L
2	0,033 mg/L	0,005 mg/L
3	0,032 mg/L	0,005 mg/L

Table 1. Analysis Results of Mercury Levels in River Water

The data above showed that the results of measuring Hg levels at several sampling points of Pesanggaran river water contained concentrations of 0.031 to 0.033 mg/L. This showed that the mercury level in the river water was above the threshold, where according to the Regulation of the Indonesian Ministtry of Health Number 416/Menkes/PER/IX/1990 the normal value of Hg in river water is 0.005 mg/L (Prayogo, 2020). It can be seen that the river water in this area is polluted and it is not recommended to use as drinking water, bathing, cooking or washing. However, it is necessary to analyze Hg levels using other methods, such as the AAS (Atomic Absorption Spectroscopy) method which is more expensive but with more accurate results obtained.

4. CONCLUSION

Based on the research result, the following conclusions were obtained:

- 1. The optimum pH value obtained when measuring Hg with UV-Visible Spectrophotometer was pH = 5.
- 2. The Hg level in river water around the gold mining area of Pesanggaran Village, Banyuwangi Regency with UV-Visible Spectrophotometer, ranged from 0.031 to 0.033 mg/L.
- 3. The Hg level of river water in this area was above the threshold and it is not recommended to use as drinking, bathing, cooking or washing.

5. SUGGESTION

The suggestion from the research result that it is necessary to analyze Hg levels using other methods, such as the AAS (Atomic Absorption Spectroscopy) method which is more expensive but with more accurate results obtained.

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REFERENCES

- Auliyah, R., Mulyasari, T.M., Purnomo, B.C., 2019, Kadar Logam Berat Merkuri (Hg) Pada Kerang Hijau Di Purwokerto Kabupaten Banyumas Tahun 2018. Bul. Keslingmas 38, 199–203. https://doi.org/10.31983/keslingmas.v38i2.4878
- [2] Ayuningtyas, I.N., Yunita, E.P., 2014, Pembuatan dan Optimasi Elektroda Selektif Ion Merkuri Berbasis Kitosan untuk Mengukur Kadar Merkuri dalam Sediaan Kosmetik 1, 10-20.
- [3] Febrianti, I., Ratianingsih, R., Puspita, J.W., 2018, Perubahan Distribusi Merkuri (Hg) Terhadap Waktu di Sedimen Sungai Poboya. J. Ilm. Mat. dan Terap. 15, 86–97. https://doi.org/10.22487/2540766X.2018.v15.i1.10205
- [4] Huljani, M., Rahma, N., 2019, Analisis Kadar Klorida Air Sumur Bor Sekitar Tempat Pembuangan Akhir (TPA) II Musi II Palembang dengan Metode Titrasi Argentometri. ALKIMIA J. Ilmu Kim. dan Terap. 2, 5–9. https://doi.org/10.19109/alkimia.v2i2.2987
- [5] Kustiningsih, Y., Fitriyanti, N., Nurlailah, N., 2017, Kadar Logam Timbal (Pb) dalam Darah Penjual Klepon. Med. Lab. Technol. J. 3, 47. https://doi.org/10.31964/mltj.v3i2.168
- [6] Maddusa, S.S., Paputungan, M.G., Syarifuddin, A.R., Maambuat, J., Alla, G., (2017). Kandungan Logam Berat Timbal (Pb), Merkuri (Hg), Zink (Zn) dan Arsen (As) Pada Ikan dan Air Sungai Tondano, Sulawesi Utara 7-27.

- [7] Mahmud, M., Lihawa, F., Isa, I., Patuti, I.M., 2020, Fitoremediasi Sebagai Alternatif Pengurangan Limbah Merkuri Akibat Penambangan Emas Tradisional di Ekosistem Sungai Tulabolo Kabupaten Bone Bolango. 12-22.
- [8] Nasir, M., 2018, Analisis Perbandingan Kadar Timbal (Pb) dan Besi (Fe) dalam Darah Petugas Parkir Ruang Terbuka dengan Ruang Tertutup. J. Media Anal. Kesehat. 1. https://doi.org/10.32382/mak.v1i1.196
- [9] Nuryono, N., Qomariyah, A., Kim, W., Otomo, R., Rusdiarso, B., Kamiya, Y., 2019, Octyl and Propylsulfonic Acid Co-Fixed Fe3O4@SiO2 as a Magnetically Separable, Highly Active and Reusable Solid Acid Catalyst in Water. Mol. Catal. 475, 110248. https://doi.org/10.1016/j.mcat.2018.11.019
- [10] Ohi, S., Kunusa, W.R., Lukum, A., 2020, Kadar Fe(III) pada Air Sumur Galian yang Dikonsumsi Masyarakat Menggunakan Spektrofotometer UV-VIS. Jambura J. Chem. 2, 62–69. https://doi.org/10.34312/jambchem.v2i2.4521
- [11] Pratiwi, D., Aida, E.R., 2018, Studi Penyebaran Kontaminan Logam Berat Timbal (Pb) dan Merkuri (Hg) dari Air Lindi Terhadap Air Sungai (Studi Kasus TPA Regional Kota Solok).
 J. Pendidik. Teknol. Kejuru.
 1, 167–171. https://doi.org/10.24036/jptk.v1i4.2823
- [12] Prayogo, T.B., 2020, Analisis Kualitas Air dan Strategi Pengendalian Pencemaran Air Sungai Metro di Kota Kepanjen Kabupaten Malang 10-20.
- [13] Qomariyah, A., 2014, Desorpsi Campuran Au(III) dan Cu(II) dari Magnetit Terlapis Hibrida Merkapto-Silika dengan Larutan Tiourea dalam Asam Klorida. Skripsi. Universitas Gadjah Mada.
- [14] Qomariyah, A., Hidayah, R., 2021, Abu Limbah Sekam Padi sebagai Bioadsorben yang Efektif untuk Logam Timbal dalam Tanah. Fullerene Journal of Chemistry. 81-86.
- [15] Qomariyah, A., Nuryono, N., Kunarti, E.S., 2021, Recovery of Gold in Au/Cu/Mg System from SH/Fe3O4@SiO2 as a Magnetically Separable and Reusable Adsorbent. Indones. J. Chem. Res. 9, 26–34. https://doi.org/10.30598//ijcr.2021.9-ani
- [16] Rai, I.B., (2019). Studi Kualitas Air Secara Fisika dan Kimia Sungai Ancar Kota Mataram. J. Pengabdi. Masy. Sasambo 1, 17. https://doi.org/10.32807/jpms.v1i1.371
- [17] Subhi, M., Sumijanti, E., 2021, Analisa Kualitas Air Sumur Bahan Pembuatan Keramik dengan Parameter Fisik (Suhu) Dan Kimia (Klorida) di PT. Sumber Keramik Indah Kota Probolinggo. Tesis. 41-89.
- [18] Susanti, R., Mustikaningtyas, D., Sasi, F.A., 2014, Analisis Kadar Logam Berat pada Sungai di Jawa Tengah. 12, 7.
- [19] Suteja, Y., Purwiyanto, A.I.S., Agustriani, F., 2018, Merkuri (Hg) di Permukaan Perairan Muara Sungai Banyuasin, Sumatera Selatan, Indonesia. J. Mar. Aquat. Sci. 5, 177. https://doi.org/10.24843/jmas.2019.v05.i02.p03
- [20] Trisna, Y., 2018, Water Quality and Public Health Complaints in Surrounding Watoetoelis Sugar Mills. J. Kesehat. Lingkung. 10, 241. https://doi.org/10.20473/jkl.v10i2.2018.241-251